

STUDIES OF QUASI-PARTICLE PROPERTIES IN SOLIDS

ULF von BARTH



Department of Theoretical Physics
University of Lund

Lund, Sweden

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by

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The present paper is an introduction to and summary of a thesis comprising the following five papers:

- A. U. von Barth and L. Hedin: A local exchange-correlation potential for the spin polarized case: I, Journal of Physics C: Solid State Physics 5, 1629-1642 (1972)
- B. G. Arbman and U. von Barth: Quasi-Particle Energies in Aluminium, Il nuovo Cimento 23 B, 37-50 (1974)
- C. G. Arbman and U. von Barth: Correlated Potentials for Simple Metals: Aluminium, submitted to the Journal of Physics C: Solid State Physics
- D. C.O. Almbladh and U. von Barth: Non-Linear Screening of a Fixed Point Charge in an Electron Gas, to be published.
- E. C.O. Almbladh and U. von Barth: The Spherical Model: An Application to X-ray Edges in Li, Na and Al, to be published



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Introduction

In classical mechanics the motion of a particle subject to a force can be obtained from Newton's second law provided we know the velocity and the position of the particle at one instant of time. Newton's second law simply states that the force is proportional to the acceleration of the particle, and the constant of proportionality is called the mass of the particle. Thus Newton's second law is just a precise way of formulating our every-day knowledge of the forces and velocities we experience e.g. in driving a car, skiing or running. Turning to the microscopic world of the small particles that are the constituents of matter, this knowledge is of little guidance, and we must resort to quantum mechanics. All our present-day understanding of the microscopic properties of solid matter is based upon the theory of quantum mechanics.

From this theory we learn that questions such as "Where is the particle?" or "What velocity does it have?" are ill-posed. Instead, all the properties of the particle are described by a function Ψ of space ($\vec{r}$) and time (t), and the analog of Newton's second law is a differential equation, the famous Schrödinger equation, obeyed by the function Ψ .

$$\left\{ -\frac{1}{2m} \nabla^2 + V(\vec{r}) \right\} \Psi(\vec{r}, t) = i \frac{\partial}{\partial t} \Psi(\vec{r}, t) \quad (1)$$

The mass of the particle is m and the so called potential $V(\vec{r})$ is related to the force acting on the particle in a simple way which was known already in classical mechanics. The quantum mechanical analog of the question "Where is the particle?" is now "What is the probability of finding the particle in a small volume v around the point $\vec{r}$ in space at time t ?", and the answer is $|\Psi(\vec{r}, t)|^2 \cdot v$. Similarly, the velocity of the particle

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has a probability distribution simply related to Ψ .

Quantum mechanics being a theory encompassing classical mechanics must, however, have features with no classical analog. One such is the notion of stationary states. When the particle is in a stationary state its probability distribution $|\Psi|^2$ is independent of time and writing $\Psi(\vec{r}, t) = \varphi(\vec{r}) \cdot \exp(-iEt)$ for Ψ the time dependent Schrödinger equation is replaced by

$$\left\{ -\frac{1}{2} \nabla^2 + V(\vec{r}) \right\} \cdot \varphi(\vec{r}) = E\varphi(\vec{r}) \quad (2)$$

where E now has the precise meaning of the energy of the particle. The simplest possible realistic problem in non-relativistic quantum mechanics is the hydrogen atom, in which a negatively charged electron is orbiting around a positively charged proton due to the attraction between charges of opposite sign. Simple electrostatics tells us that $V(\vec{r})$ is inversely proportional to the distance between the two particles, and since the proton is much heavier than the electron the proton can be considered to be at rest and the Schrödinger equation (2) for the electron can be solved exactly. The helium atom has two electrons moving around a nucleus consisting of two protons and two uncharged neutrons. Again the motion of the much heavier nucleus can be disregarded, but the electrons, having the same kind of charge, will repel each other and each one of the electrons will thus feel both the attractive force of the nucleus and the repulsive force from the other electron. It turns out that the Schrödinger equation for the two electrons cannot be solved exactly although very accurate approximations are now known. The difficulty is due to the interaction between the two electrons. To obtain the probability distribution of one of the electrons, the forces acting on it must be determined, and since part of this force stems from the other electron its probability distribution must also be determined, a problem as difficult as the one with which we started.

In a solid there are 10^{23} nuclei and many more electrons. Every electron in the solid experiences an attraction to each

nucleus and a repulsion from every other electron, and the problem appears to be completely intractable. On the other hand, a solution to the problem would enable us to answer many interesting questions such as "Why is copper red?", "Why is aluminium a good conductor?", "Why is silicon a semiconductor?", "What energy does it require to split a piece of solid iron into iron atoms?" or "How are the electrons distributed in a piece of solid lithium?" Using an approach which is physically very appealing, one was able to obtain qualitatively correct results already in the early thirties. The idea was to consider each of the electrons as moving in the force field of the nuclei and in an average force field of all the other electrons. Each electron thus moves in the same force field and the probability distribution $|\varphi_i|^2$ of the i :th electron can be obtained in analogy with the simple hydrogen problem by solving the Schrödinger equation

$$\left\{ -\frac{1}{2m} \nabla^2 + V_n + V_{\text{eff}} \right\} \varphi_i = E_i \varphi_i \quad (3)$$

V_n represents the force from the nuclei and V_{eff} represents the effective force from all the other electrons. The sum of the probability distribution of all the electrons is what we call the electron density $n(\vec{r})$.

$$n(\vec{r}) = \sum_{i=1}^N |\varphi_i(\vec{r})|^2 \quad (4)$$

Disregarding the fact that the so called independent particle model described above might be an oversimplification of the tremendously complicated problem of a solid, we still have to determine the form of the effective force field V_{eff} . Since the electrons are charged particles with a charge $-e$ a first ansatz was obtained by setting V_{eff} equal to the electrostatic potential V_H felt by a particle with a charge $-e$ in a charge distribution $-e n(\vec{r})$. This approximation is often referred to as the Hartree approximation, and already this

simple ansatz gives quite reasonable results for solid state properties. To improve upon the Hartree approximation one added to the effective force field V_{eff} a term V_{xc} which was intended to better account for the effect on one electron produced by the motion of all the others. In most cases this was done in a rather ad hoc manner without justification from the original Schrödinger equation of the solid. Often quite good results were obtained, the reason being that the final result for e.g. the electron density $n(\vec{r})$ or the energy of the solid is to a large extent determined by V_{n} and V_{H} , and is only weakly dependent on V_{xc} . Also, parameters were used to fit the results to experimental data.

It was not until the middle of the sixties that it was realized that there really exists a force field $V_{\text{xc}}(\vec{r})$ such that the independent particle model described above becomes an exact procedure derivable directly from the Schrödinger equation of the solid. However, the appealing interpretation of $|\varphi_i|^2$ and E_i as being the probability distribution and the energy of the i :th electron must now be abandoned, and only the sum of the $|\varphi_i|^2$'s and the sum of the E_i 's have physical meaning as the electron density and part of the energy of the solid. Furthermore, the exact form of V_{xc} is now known for a system with a very slowly varying electron density, and this form can be used approximately in the real solid as well. In paper D of the present thesis we have used this form of V_{xc} to obtain the electron density for a simplified model of a metal in which all nuclear matter except for one proton is uniformly spread out over the solid. This model, referred to as an electron gas with an impurity, has no direct relevance to a real metal but is a prototype for more realistic descriptions. The model has been used for many years by the physicists as a testing ground for different approximations, but the electron density obtained by us is probably the most accurate so far. Our results show the striking feature that the piling up of the electrons around the proton is rather independent of the number of electrons per unit volume appropriate to real metals.

Another feature of quantum mechanics that has no classical analog is the so called spin of a particle. It can be pictured as a kind of angular momentum originating in the rotation of the particle about its own axis. However, along any given direction the spin of an electron can only be either up or down, an extremely peculiar property from the point view of everyday experience. Nevertheless the phenomenon of ferromagnetism is due to the presence of an unequal number of spin up and spin down electrons in a solid. Magnetism is thus purely a quantum mechanical phenomenon. A ferromagnetic solid can be thought of as containing two different kinds of electrons, spin up and spin down electrons with their respective spin up and spin down electron densities. If these densities are known the magnetization of the solid can be calculated. It is the purpose of the first paper of the present thesis to prove that these densities are exactly obtainable, in the independent particle model, from two Schrödinger equations with two exact force fields V_{xc}^{up} and V_{xc}^{down} acting on the spin up and spin down electrons respectively. In analogy with the corresponding theorem for the non-magnetic case discussed previously we also obtain exact expressions for V_{xc}^{up} and V_{xc}^{down} for a system with a very weak spatial variation of the spin up and spin down densities. These expressions which are approximate in a real solid are presently being tested in the calculation of the static magnetic properties of solids.

There are two fundamental disadvantages with the exact independent particle approach. (i) Only approximations to the exact potential V_{xc} are presently known and there is no systematic way by which they can be improved. An exact determination of V_{xc} is just as difficult as solving the full Schrödinger equation of the solid. (ii) Even if we knew the exact V_{xc} we can only obtain the electron density and the energy of the solid. Interesting questions such as how the solid reacts when it is exposed to light, whether it is a good conductor or a poor or even a semiconductor or an insulator, are outside the scope of the theory.

To answer questions of this kind we would like to know how single electrons react under external forces i.e. we would like to return to the old interpretation of the $|\varphi_i|^2$'s and E_i 's as the probability distributions and energies of the single electrons. However, from the modern theory of many-body physics we learn that due to the strong interactions between the electrons the concept of independent particles is of very limited validity. Instead we are led to the concept of a quasi-particle, which can be considered as an aggregate of an electron and the hole in the electron density that is created in the vicinity of the electron, due to the repulsion of the other electrons. Because a lack of electrons is equivalent to a positive charge these quasi-particles are rather neutral objects that interact much more weakly. Furthermore one can prove that the energies E_i of these quasi-particles can be obtained exactly from a Schrödinger-like equation similar to that of the independent particle approximation

$$\left\{ -\frac{1}{2} \nabla^2 + V_n + V_H + \Sigma(E_i) \right\} f_i = E_i f_i \quad (5)$$

The quantity V_{xc} of the independent particle model has been replaced by the much more complicated quantity Σ which is called the self-energy of the electrons. Σ depends on the energy E_i of the quasi-particle i and is thus different for quasi-particles of different energies. Moreover, Σ is what is known among physicists as a non-local operator, which means that Σ also depends on the form of the entire function f_i . Unfortunately the $|f_i|^2$'s cannot be interpreted as the probability distribution of the quasi-particles and because the quasi-particles are objects consisting of many electrons moving in a coordinated way, the sum of the $|f_i|^2$'s is no longer the electron density, a mistake sometimes seen in the literature. The energies E_i , on the other hand, are directly connected to measurable quantities. These energies determine e.g. the smallest energy required to take one electron out of the solid and the energy required to take out of the solid one of those electrons that are very closely bound to one of the nuclei. They determine the wavelength of

the light that is on the edge of being able to shine through the solid. Other characteristic structure in the ability of the solid to absorb and reflect light is also to be obtained from the energies E_i . In order to calculate these energies we must solve Eq.(5) and for this we need to know the self-energy Σ . To obtain Σ is again as difficult, in principle, as to solve the full Schrödinger equation of the solid. However, one of the great achievements of many-body theory is the development of a systematic scheme of successive approximations for Σ . These approximations often have a simple interpretation in physical terms and are thus easy to understand. In the papers B and C of the present thesis such approximations are discussed and applied in a calculation of the quasi-particle energies in aluminium. The results compare as favourably as previous more phenomenological theories, to the experimental results, but our approach yields much more insight into the problems and the road to further improvements lies open.

In paper E of the present thesis a slightly different approach was taken to calculate the energy of a quasi-particle which is very tightly bound to one of the nuclei. These quasi-particles are very localized around a specific nucleus and we showed that for such electrons the methods developed in paper C and D were not sufficient. The energies of tightly bound quasi-particles are large and give the position of pronounced structure in X-ray spectra of solids. Our theory is able to predict the experimentally obtained positions with a high accuracy.

To explore the full consequences of the theories laid down in the present thesis there remains much more hard computational work to be carried out. I believe the underlying physical principles to be sound and expect that further computational work will lead to still better agreement with experimental results. It should be kept in mind that there are many interesting properties of a solid that cannot be described in quasi-particle terms, but these properties lie outside the scope of the present thesis.

Summary of papers

A. The local density theory of Hohenberg, Kohn and Sham is extended to the spin-polarized case and explicit local spin-dependent one-particle potentials are obtained from a generalized random phase approximation for the spin-split homogeneous electron gas. The potentials can be used in the spin-split band calculations for the determination of ground state magnetic properties of solids. The long wave length spin susceptibility of an electron gas is also calculated and compares favourably to previous results and experiments.

B. A potential for the calculation of quasi-particle energies in simple metals is constructed from first principles. It is based on the dynamically screened exchange approximation for the self-energy. The essential features are: (i) the core-valence exchange interaction is treated exactly, (ii) for the valence-valence exchange and correlation interaction we use the Sham-Kohn local density approximation for the self-energy, (iii) the core polarization potential is obtained from spectral data for the ion, and this potential is not screened in the core region (iv) the Coulomb potential is taken from an electron charge density obtained from a self-consistent Kohn-Sham ground state calculation in the muffin-tin approximation. The results compare well with previous calculations and semiempirical fits and indicate that the occupied quasi-particle levels in aluminium can be found from a priori theory to within an accuracy of ~ 0.1 eV.

C. This paper is an extended version of paper B. A more detailed description of how to construct a quasi-particle potential is given and the relation to experiments is discussed. The low frequency optical absorption is calculated.

D. The charge density and the relaxation energy of an electron gas with a fixed positive unit point charge is calculated for metallic densities by means of self-consistent Kohn-Sham ground state calculations. The results differ markedly from the case

of linear screening especially at lower densities. The screening length is found to be almost constant for metallic densities in contrast to previous estimates. Bound states appear already in the beginning of the metallic density range but have no drastic effect on the electron density. An error in an earlier work by Kohn and Majumdar on this subject, is pointed out.

E. To treat excitations localized to one site in a solid, a simple spherical model has been developed. The potential on the surrounding sites are turned into pseudo atom potentials and only the spherical average of the sum of these potentials is retained. The model is used to calculate X-ray threshold energies from both singly and doubly ionized core levels and self-consistent calculations are made for the ground state and for the states containing one and two core holes. The threshold energies are obtained from differences in total energies and the agreement with the corresponding experimental energies is generally better than .5 eV.

The model is discussed from the stand point of self-energy calculations.

We also calculate phase shifts relevant to the Nozieres-De Dominicis theory and our results suggest a revision of the present form of the many-body theory of X-ray edges.

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